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Technical Report No. 1

"Synthesis and Structural Characterization of Pt-Si Dimers
with Unusually Short Cross-Ring Silicon-Silicon Interactions"

by

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Published

in the

Journal of the American Chemical Society

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May 5, 1989

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Synthesis and Structural Characterization of Pt-Si Dimers with Unusually Short Cross-Ring Silicon-Silicon Interactions

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Received November 5, 1987

Polysilanes have use in applications where photosensitivity is required and as precursors to β -SiC.¹ Polysilanes are usually prepared from dichloroorganosilanes and sodium at $\approx 100^\circ\text{C}$.² Several reports of transition-metal-catalyzed formation of polysilanes from R_2SiH_2 and RSiH_3 have appeared in which product distributions have been the main focus.³ The mechanism of this

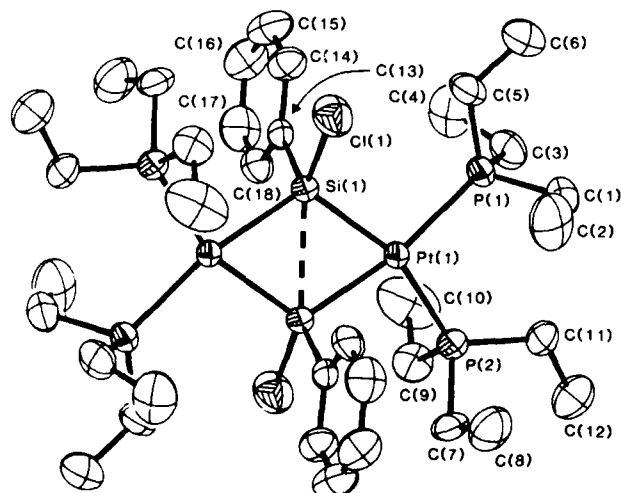
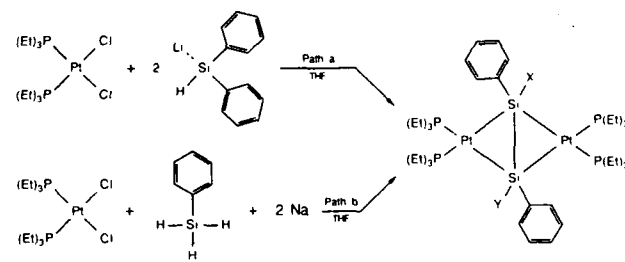


Figure 1. ORTEP labeling diagram of 1a-c and 1b. The thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity.

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Scheme 1^a



^a 1a, X = Y = H; 1b, X = Y = Cl; 1c, X = H, Y = Cl.

catalytic process is poorly understood.^{2b,4,5} Dimeric silyl- or hydride-bridged complexes of titanium and zirconium are the only reported metal-containing species isolated from catalytic silane polymerizations.⁶ Herein we report the synthesis and structural characterization of a series of platinum-silyl dimers with unusually short cross-ring Si-Si distances. These dimers are catalysts or catalyst precursors in silane oligomerization reactions.

The preparation of cocrystallized mixtures of three platinum-silyl dimers $[(\text{Et}_3\text{P})_2\text{Pt}(\text{SiPhX})(\text{SiPhY})\text{Pt}(\text{PEt}_3)_2]$ (1a, X = Y = H; 1b, X = Y = Cl; and 1c, X = H and Y = Cl) from two very different reaction paths is shown in Scheme 1. The reaction of $\text{PtCl}_2(\text{PEt}_3)_2$ with LiSiHPh_2 in THF (path a, Scheme 1) yields a small quantity of the cocrystallized mixture 1a-c as air stable yellow crystals suitable for X-ray diffraction studies. The complexes 1a-c are the major platinum-containing products produced by the reaction of $\text{PtCl}_2(\text{PEt}_3)_2$ with SiH_3Ph in THF with the addition of a slight excess of sodium powder (path b, Scheme 1).⁷

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(5) $\text{PtCl}_2(\text{PEt}_3)_2$ was prepared from $\text{PtCl}_2(\text{NC-Ph})_2$ and PEt_3 . Its properties were as reported by Jensen (Jensen, K. A. Z. *Anorg. Allg. Chem.* **1936**, 229, 225-281).

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(7) All reactions were conducted under an argon atmosphere. The product from path a was obtained by removing the THF under vacuum followed by extraction with and recrystallization from hexane. The reaction mixture of path b showed the evolution of gas, presumably H_2 . Filtration of the mixture and removal of the solvent leaves a dark brown oil which when quickly washed with acetone yields the yellow solid 1a-c. Low isolated yields (10-20%) of pure 1a-c from path b are due to reaction of acetone with 1a-c and to difficulties in completely removing traces of the liquid oligomeric silanes from 1a-c via subsequent recrystallizations from hexane.

Crystals of pure **1b** can be obtained by treating toluene solutions of **1a-c** with carbon dioxide followed by recrystallization from benzene. Apparently the Si-H bonds of **1a** and **1c** react with carbon dioxide to yield unidentified complexes, whereas **1b** is unreactive.

Both paths a and b in Scheme 1 are complicated by partial chlorination of the Si-H bonds. This is not unexpected because Noble metals catalyze chlorination of Si-H bonds using a variety of chloride sources.⁸ Path a proceeds with the net loss of a phenyl substituent. We have not determined whether this can be attributed to a metal-catalyzed disproportionation of the substituents^{2a,d,3a,9,10} or to rearrangement of the silyllithium reagent.¹¹

The addition of catalytic quantities of **1a-c** to phenylsilane yields di- and trisilanes, with some scrambling of the phenyl and hydride substituents.¹² The di- and trisilanes are also produced by the addition of $\text{PtCl}_2(\text{PEt}_3)_2$ to excess SiH_3Ph and are byproducts of path b.¹²

Field desorption mass spectrometry of **1a-c** clearly shows that all three dimers are present in the crystalline compound. The X-ray study of the product from path a was performed.¹³ Alternating refinements to convergence holding the thermal parameters of the chlorine atom fixed while the occupancy factor was freed and vice versa shows that a silyl chloride is present in place of a silyl hydride approximately 65% of the time in this particular crystalline mixture.¹³ Pure **1b** has also been crystallographically characterized.¹⁴ All products were further characterized by IR and NMR spectroscopy.^{15,16}

An ORTEP drawing of the structure of **1a-c** and pure **1b** is shown in Figure 1. The silicon atoms and H or Cl and phenyl substituents lie in a plane which is perpendicular to the Pt-Pt vector and the plane defined by the platinum-silicon ring. The Si-Si separations in **1a-c** (2.575 (15)–2.602 (4) Å) are within the range of known single Si-Si bonds (2.33–2.70 Å)¹⁷ and are the shortest cross-ring Si-Si distances in any metal-silicon four-membered ring.^{18–20} The Pt-Si bonds (2.355 (7)–2.383 (8) Å) are long when compared to other Pt-Si bonds in environments of similar steric demands.^{10,18} The acute deviation of the angle at the "square-planar" platinum atoms (Si-Pt-Si = 65.9 (3)–66.5 (1)°) and the increase in the angles of the "tetrahedral" silicon atoms (Pt-Si-Pt = 113.6 (1)–114.2 (3)°) suggest that the Si-Si interaction forms

an integral part of the bonding scheme. The acute Si-Pt-Si angle is not a result of van der Waals repulsions between the platinum atoms because the Pt-Pt distances range from 3.973 (1)–3.997 (2) Å, whereas platinum has a van der Waals radius of 1.7–1.8 Å.²² The large cross-ring Si-Si separations (3.852–4.225 Å),²¹ acute M-Si-M angles (69.6–75.0°), and short M-M distances (2.708–3.183 Å) of most other metal-silicon dimers are in sharp contrast to those of **1a-c**.^{10,18–20} Only $[\text{Cp}_2\text{TiSiH}_2]_2$ has a similar cross-ring Si-Si distance (2.69 Å)²⁰ and M-Si-M angle (103°).²⁰

The π -coordination of the disilene $\text{Ph}_2\text{Si}=\text{SiPh}_2$ to two Pt-(PEt₃)₂ moieties provides a bonding picture of the complexes **1a-c** which is consistent with their geometry. This bonding picture of **1a-c** has been supported by a recent theoretical investigation.²³ The π -coordination of a bulky disilene to a single platinum has been reported, but crystallographic data are not available.²⁴ As a consequence of π -coordination, the Si-Si distance of **1a-c** is lengthened by 19–22% from that in free disilenes (2.13–2.16 Å).²⁵ This percent lengthening can be compared to the 12% or 27% lengthening of the C-C distance in $\text{CH}_2=\text{CH}_2$ on π -coordination to two zirconium centers in $\text{Zr}_2\text{X}_6(\text{PEt}_3)_4(\text{CH}_2=\text{CH}_2)$ (X = Br or Cl, respectively).²⁶ In **1a-c** and $\text{Zr}_2\text{X}_6(\text{PEt}_3)_4(\text{CH}_2\text{CH}_2)$ the resultant Si-Si (2.58–2.60 Å) or C-C (1.56 and 1.69 Å) separations are longer than the "typical" single bond distances (Si-Si = 2.34 Å and C-C = 1.54 Å).²² The bonding descriptions of **1a-c** and the zirconium-ethylene complexes²⁶ are extensions of the Dewar-Chatt-Duncanson (DCD) model, which recently has also been applied to the cross-ring Si-Si interactions in $[\text{R}_2\text{SiX}]_2$ (X = CH₃, NH, O, PH, or S).²⁷ The chemistry of **1a-c** shows similarities to that of π -coordinated diphosphene complexes because the synthesis of $\text{M}(\eta^2\text{-RP}=\text{PR})\text{L}_n$ can involve monophosphorus reagents^{28,29} and similar DCD bonding schemes have been developed.²⁹ As a consequence of the bonding scheme the silicon atoms of **1a-c** are pentacoordinated in a highly distorted trigonal bipyramidal geometry.^{30,31} Placing the platinum atoms in the axial positions is consistent with the relatively long Pt-Si bonds,³⁰ and this results in positioning the hydrides in their favored

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(12) Determined by FD-MS, IR, and NMR data.

(13) (a) Crystallographic data for **1a-c**: space group, $P2_1/n$, $a = 10.985$ (2) Å, $b = 11.803$ (2) Å, $c = 17.636$ (3) Å, $\beta = 99.62$ (2)°, $V = 2254.4$ (8) Å³, and $Z = 2$. Intensity data were collected from $3.0 < 2\theta < 50.0^\circ$. Refinement on the basis of 1946 reflections ($I \geq 3\sigma$) resulted in a final $R = 0.068$ and $R_w = 0.070$. (b) UCLA Crystallographic Computing Package, December 2, 1985. Numerical absorption correction was applied.

(14) Crystallographic data for **1b**: space group $P2_1/n$, $a = 10.962$ (2) Å, $b = 11.833$ (2) Å, $c = 17.609$ (4) Å, $\beta = 99.62$ (2)°, $V = 2252.2$ (8) Å³, and $Z = 2$. Intensity data were collected from $3.0 < 2\theta < 52.0^\circ$. Refinement on the basis of 4116 reflections ($I \geq 3\sigma$) resulted in a final $R = 0.054$ and $R_w = 0.043$. See ref 13b.

(15) Selected spectral data for the mixture **1a-c**: IR (Nujol mull) $\nu_{\text{Si-H}} = 1955$ (m) and 1980 (m) cm^{-1} ; ^1H NMR (C_6D_6) 0.85 (m, CH_3), 1.72–1.83 (m, CH_2), 4.37 (m, SiH), 7.25, 7.71, and 7.94 (t, d, and d, respectively, C_6H_5). Except for the absence of the Si-H signals, the IR and NMR data for **1b** are virtually identical with those of **1a-c**.

(16) Hydride bridges on the metal-silicon bonds are a common feature in the structures of metal-silicon four-membered rings.¹⁰ We find no evidence of such in the crystallographic or spectra data of **1a-c** or **1b**.

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(21) Cross-ring Si-Si separations and other parameters were calculated by us with data provided in the original reference.

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equatorial sites.³² The inclusion of the Si-Si bond in two fused three-membered rings can help explain its length.³³

Acknowledgment. We thank Dr. William Kroenke of BFGoodrich Co. for mass spectra, Professor Robert West for providing information prior to publication, and the Office of Naval Research for support.

Registry No. **1a**, 113999-66-9; **1b**, 113999-67-0; **1c**, 113999-68-1; $\text{PtCl}_2(\text{PEt}_3)_2$, 15390-95-1; LiSiHPh_2 , 17950-77-5; PhSiH_3 , 694-53-1.

Supplementary Material Available: Tables of data collection and refinement details, atomic positional parameters, thermal parameters, and bond lengths and angles for the cocrystallized dimers **1a-c** and dichloride dimer **1b** (10 pages); observed and calculated structure factors for **1a-c** and **1b** (27 pages). Ordering information is given on any current masthead page.

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